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(54) Exhaust gas purification catalyst

(57) An exhaust gas is cleaned using a catalyst supported by a heat-resistant filter such as a cordierite honeycomb. The catalyst consists essentially of Cs, Cu and at least one of Ce and La for oxidizing fine carbonaceous particles in the exhaust gas and simultaneously reducing nitrogen oxides with the fine carbonaceous particles as a reducing agent. Silver is optionally present.

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EXHAUST GAS CLEANER

The present invention relates to an exhaust gas cleaner and a method of cleaning an exhaust gas by using such an exhaust gas cleaner, and more particularly to an exhaust gas cleaner comprising  
5 a filter carrying a catalyst and a method of cleaning an exhaust gas from diesel engines, etc. by using this exhaust gas cleaner.

Recently, nitrogen oxides and fine carbonaceous particles (mainly composed of fine, solid carbon particles, and fine, liquid or  
10 solid high-molecular weight hydrocarbon particles) contained mainly in exhaust gases of diesel engines have been causing environmental problems. Since these fine carbonaceous particles have an average particle size of 0.1-1  $\mu\text{m}$ , the fine carbonaceous particles are likely to float in the air and be inhaled by breathing. In addition, a recent clinical test has shown  
15 that the fine carbonaceous particles contain carcinogens.

The removal of these fine particles is generally carried out by one of the following two methods: One method comprises passing the exhaust gas through a heat-resistant filter to trap the fine particles, and burning the trapped fine particles by a burner, an electric heater,  
20 etc. when pressure loss has increased to a certain level, thereby regenerating the filter. Such a filter may be a metal wire mesh, a ceramic foam, a monolithic ceramic honeycomb, etc. Another method comprises using a heat-resistant filter carrying a catalytic material for performing both filtration and burning actions, thereby reducing the  
25 frequency of burning fine particles and regenerating the filter. By increasing the activity of the catalyst, the regeneration of the filter can be omitted.

Attempts have been made in these methods to lower the ignition temperature of fine particles by increasing the percentages of combustible components in the exhaust gas, or by adding a carbonaceous oxidation accelerator to a fuel.

5 In the former method, as the removal effect of fine particles increases, the pressure loss takes place more quickly, and so the regeneration of the filter should be conducted more frequently. In addition, the regeneration needs to have high reliability, meaning that this method is economically disadvantageous.

10 On the other hand, the latter method would be considered to be an excellent method if there is a catalyst capable of maintaining its activity at exhaust gas conditions of diesel engines (gas composition and temperature). However, the exhaust gas temperatures of diesel engines are relatively lower than those of gasoline engines. In  
5 addition, since a gas oil is used as a fuel in diesel engines, the exhaust gases contain a large amount of  $\text{SO}_2$ . Nevertheless, there has been no established method of well igniting and burning fine carbonaceous particles accumulated under these exhaust gas conditions without causing secondary pollution.

0 For instance, when base metal catalysts are supported on filters, the fine carbonaceous particles are ignited at as high a temperature as  $350^\circ\text{C}$  or higher. However, for most of the usual operations of diesel engines, etc., the exhaust gas temperature is lower than the above temperature, failing to cause a combustion reaction. As  
5 a result, fine particles are trapped by a catalyst-carrying filter and then burned when the temperature has increased to a certain level, thereby regenerating the filter. In this case, the pressure loss increases quickly until the filter reaches a certain temperature,

necessitating the frequent burning and regeneration by a burner, an electric heater, etc. This is a practical disadvantage. When a catalyst containing precious metals is used, the fine particles are likely to be burned at a lower temperature, reducing the rate of increase of the pressure loss. However, the oxidation of  $\text{SO}_2$  in the exhaust gas takes place simultaneously. As a result, extremely harmful  $\text{SO}_3$  and sulfuric acid mist are generated, causing secondary air pollution.

As mentioned above, there has been no known method of efficiently removing the fine carbonaceous particles from the exhaust gas discharged from diesel engines, etc. In addition, it is extremely difficult to remove nitrogen oxides from the exhaust gas whose oxygen concentration varies in a wide range of 2-20%.

Japanese Patent Laid-Open No. 63-242346 discloses a method of removing fine carbonaceous particles and nitrogen oxides from exhaust gas by using a heat-resistant filter carrying a catalyst comprising alkali metals and transition metals. However, even by this method, the removal ratio of nitrogen oxides at an exhaust gas temperature of about  $300^\circ\text{C}$  is less than 20%. Accordingly, the development of better catalysts has been desired.

Accordingly, an object of the present invention is to provide an exhaust gas cleaner capable of not only effectively burning fine carbonaceous particles contained in the exhaust gas having a relatively large oxygen concentration variation at a relatively low temperature such as those of diesel engines, but also effectively removing nitrogen oxides by reaction with the fine carbonaceous particles.

Another object of the present invention is to provide a method of cleaning an exhaust gas by using such an exhaust gas cleaner.

5 In view of the above objectives, the inventors have investigated a reaction between fine carbonaceous particles, oxygen and nitrogen oxides in the presence of a catalyst. As a result, it has been found that a combination of particular elements in group IA (alkali metals), the group IB (transition metals), and the rare earth metal group is effective as a catalyst for cleaning the exhaust gas,  
10 when supported by a heat-resistant filter. The present invention is based on this finding.

Thus, the exhaust gas cleaner according to the present invention comprises a heat-resistant filter and a catalyst supported by the filter, the catalyst comprising Cs, Cu and at least one of  
5 Ce and La.

The method of cleaning an exhaust gas according to the present invention comprises using a catalyst supported by a heat-resistant filter, the catalyst comprising Cs, Cu and at least one of Ce and La for oxidizing fine carbonaceous particles in the  
0 exhaust gas and simultaneously reducing nitrogen oxides with the fine carbonaceous particles as a reducing agent.

The exhaust gas cleaner according to the present invention  
5 comprises a heat-resistant filter and a catalyst supported thereby. The heat-resistant filter used in the present invention is disposed in an exhaust gas passage of a diesel engine. The catalyst for removing nitrogen oxides together with fine

carbonaceous particles preferably consists of Cs, Cu and at least one of Ce and La. However, this catalyst may further contain Ag.

Since the fine carbonaceous particles are brought into contact with catalyst elements and oxygen on the filter, the ignition temperature of the fine carbonaceous particles decreases so that they are burned (oxidized) at 300°C or lower. Simultaneously the fine carbonaceous particles serve as a reducing agent to reduce nitrogen oxides. Thus, by using a catalyst consisting essentially of Cs, Cu and at least one of Ce and La, the fine carbonaceous particles are activated by oxygen contained in the exhaust gas at 300°C or lower, so that they can react with nitrogen oxides. As a result, nitrogen oxides are reduced to N<sub>2</sub>, and simultaneously the fine carbonaceous particles are oxidized to CO<sub>2</sub>. Accordingly, the cleaning of the exhaust gas can be achieved at a temperature of 300°C or lower.

The heat-resistant filter is required to have necessary fine carbonaceous particle -trapping capacity while causing pressure drop within the permitted range. It is thus preferably constituted by ceramic fibers, a ceramic foam, a ceramic monolith, etc. usually used as a catalyst carrier, such as alumina, silica, titania, zirconia, alumina-titania, silica-titania, silica-zirconia, titania-zirconia, mullite, cordierite, etc.

The impregnation of the heat-resistant filter with the fine carbonaceous particle -removing catalyst may be conducted by a known method in which the heat-resistant filter is immersed in solutions of carbonates, nitrates, acetates, and hydroxides of such catalyst elements.

To increase the catalyst-supporting area of the filter, it is desirable that the heat-resistant filter supports the catalysts via a

porous carrier layer having a large surface area such as alumina powder, silica powder, titania powder, etc. When the carrier is used, the catalyst can be supported by the carrier by an impregnation method, a precipitation method, a sol-gel method, etc. The

5 impregnation method is as mentioned above. The precipitation method comprises the coprecipitation of catalyst metals and ceramic carrier materials by mixing aqueous solutions of salts of both materials. The sol-gel method comprises mixing an alcohol solution of  
10 a organometallic salt of carrier ceramics such as titanium alkoxide with an aqueous solution of catalyst elements and acids such as hydrochloric acid, nitric acid, etc.

The amounts of the catalyst elements may generally be expressed in terms of the amount of the carrier. Specifically, per 100 parts by weight of the carrier, Cs is 0.5 parts by weight or more,  
15 preferably 0.5-10 parts by weight, Cu is 2 parts by weight or more, preferably 2-20 parts by weight, and at least one of Ce and La is 0.5 parts by weight or more, preferably 0.5-10 parts by weight. When the amounts of these elements are smaller than the above lower limits, sufficient effects of removing both nitrogen oxides and fine  
20 carbonaceous particles cannot be achieved. The more preferred amounts are 1-5 parts by weight (Cs), 5-15 parts by weight (Cu), and 1-5 parts by weight (at least one of Ce and La).

When the catalyst contains Ag, the amount of Ag is 0.01 parts by weight or more per 100 parts by weight of the carrier,  
5 preferably 0.01-5 parts by weight. When it is less than 0.01 parts by weight, sufficient effect of lowering the ignition temperature of fine carbonaceous particles and increasing the  $\text{NO}_x$  removal ratio cannot be

achieved. The more preferred amount of Ag is 0.05-2 parts by weight or more.

Incidentally, the amount of the carrier relative to the heat-resistant filter may vary depending upon the type of the filter, but it is generally 2-15 parts by weight per 100 parts by weight of the filter.

The present invention will be explained in further detail by the following Examples.

#### Examples 1-4

A commercially available ceramic honeycomb made of cordierite having a volume of 2 l, a density of 0.37 g/ml and a porosity of 86.0% (mainly composed of magnesia, alumina and silica) was coated with titania powder (average particle size: 0.04  $\mu$ m) in an amount of 10 weight % based on the ceramic honeycomb by an impregnation method, and the resulting titania layer was impregnated with 2.5 weight % of Cs by using  $\text{CsNO}_3$ , 10 weight % of Cu by using  $\text{CuCl}_2$ , and 2.5 weight % of Ce by using  $\text{Ce}(\text{NO}_3)_3$ . The amount of catalyst element is based on the carrier. This catalyst-carrying ceramic filter was dried at 150°C or lower and then burned at 700°C for 3 hours. The resulting exhaust gas cleaner is identified as:

(Cs/Cu/Ce: Example 1)

In the same manner as in Example 1, a ceramic honeycomb filter was impregnated with 2.5 weight % of Cs, 10 weight % of Cu, and 2.5 weight % of La by using  $\text{LaCl}_3$  (Example 2).

Also, the exhaust gas cleaner of Example 1 was further impregnated with 0.5 weight % of Ag by using  $\text{AgNO}_3$  (Example 3). Similarly, the exhaust gas cleaner of Example 2 was further impregnated with 0.5 weight % of Ag (Example 4).

(Cs/Cu/La: Example 2),



(Cs/Cu/Ce/Ag: Example 3), and

(Cs/Cu/La/Ag: Example 4).

Each of the exhaust gas cleaners in Examples 1-4 was evaluated with respect to the ignition temperature of fine carbonaceous particles (expressed by temperature at which pressure drop decreases) and the removal ratio of NO<sub>x</sub> (conversion ratio of NO<sub>x</sub> to N<sub>2</sub>) by using a single-cylinder engine having a displacement of 510 cc. The engine was operated at 1500 rpm under a load of 90%. NO<sub>x</sub> concentration was about 480 ppm and oxygen concentration was 5% in the exhaust gas. The results are shown in Table 1.

Comparative Example 1

For comparison, an exhaust gas cleaner was produced from a cordierite honeycomb filter without a catalyst and measured with respect to the ignition temperature and the NO<sub>x</sub> removal ratio in the same manner as in Examples. The results are shown in Table 1.

Table 1

<u>No.</u>	<u>Ignition Temp. (°C)</u>	<u>NO<sub>x</sub> Removal Ratio at 300°C (%)</u>
Example 1	280	21
Example 2	275	20
Example 3	272	27
Example 4	267	25
Comparative Example 1	600	-

The exhaust gas cleaners of Examples 1-4 showed the ignition temperatures of 267°C-280°C and a high NO<sub>x</sub> removal ratio of 20% or more. On the other hand, NO<sub>x</sub> was not removed by the exhaust gas cleaner of Comparative Example 1.

- 5        As described above, by using the exhaust gas cleaner according to the present invention, fine carbonaceous particles and nitrogen oxides can be removed efficiently from the exhaust gas even at a relatively low temperature.

CLAIMS:

1. An exhaust gas cleaner comprising a heat-resistant filter and a catalyst supported by said filter, said catalyst comprising Cs, Cu and at least one of Ce and La.
2. An exhaust gas cleaner as claimed in claim 1 wherein said catalyst consists essentially of Cs, Cu and at least one of Ce and La.
3. An exhaust gas cleaner as claimed in claim 1, wherein said catalyst further contains Ag.
4. An exhaust gas cleaner as claimed in any one of claims 1-3 in which the heat-resistant filter supports the catalysts via a porous carrier layer.
5. An exhaust gas cleaner as claimed in claim 4, wherein said carrier comprises 0.5 parts by weight or more of Cs, 2 parts by weight or more of Cu and 0.5 parts by weight or more of Ce or La, based on the weight of the carrier.
6. An exhaust gas cleaner as claimed in claim 1 substantially as herein described with reference to any of examples 1-4.
7. A method of cleaning an exhaust gas, which method comprises passing said exhaust gas through a catalyst supported by a heat-resistant filter, said catalyst comprising Cs, Cu and at least one of Ce and La, so as to oxidize fine carbonaceous particles which are present in said exhaust gas and simultaneously reduce nitrogen oxides in the presence of said fine carbonaceous particles as a reducing agent.
8. A method as claimed in claim 7 wherein said catalyst further contains Ag.
9. A method as claimed in claim 7 substantially as herein described with reference to any of examples 1 to 4.

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